(12) UK Patent Application (19) GB (11) 2 011 309 A

(21) Application No 7847284
(22) Date of filing 5 Dec 1978
(23) Claims filed 5 Dec 1978
(30) Priority data
(31) 2755216
(32) 10 Dec 1977
(33) Fed. Rep. of Germany (DE)
(43) Application published 11 Jul 1979
(51) INT CL[2] B29D 9/00 B29F 1/10 3/00
(52) Domestic classification B5A 1R214F 1R314C1D 1R314C1F 1R314C2X 1R314C6 T14M T17P
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(58) Field of search B5A
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(54) Improving Interfacial Bond of Moulded Composite Articles

(57) A process for the manufacture of a plastics article which comprises bringing at least two plastics into contact with one another and shaping them and bonding them to one another at the contact surface, wherein at least one of the two plastics comprises components which react with one another during the shaping, at least in the region of the contact surface, and the other of the two plastics in the liquid state during the shaping, at least in the region of the contact surface, and wherein at least one of the reactive components has a pronounced tendency to diffuse into the other plastic. The diffusing component may be a monomer or low-molecular weight constituent of one plastic and a solvent for the other plastic. The composite article may be formed by injection or extrusion moulding. One plastic may be a thermosetting polyester and the other plastic may be polystyrene or polymethyl methacrylate. The polyester may be reinforced with glass fibres.

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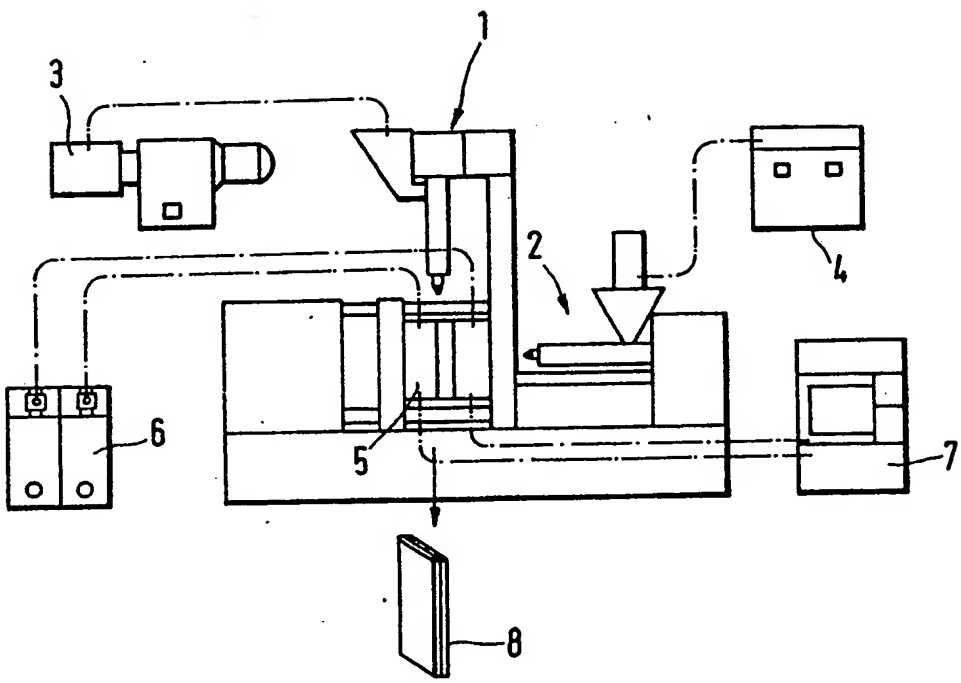

FIG. 1

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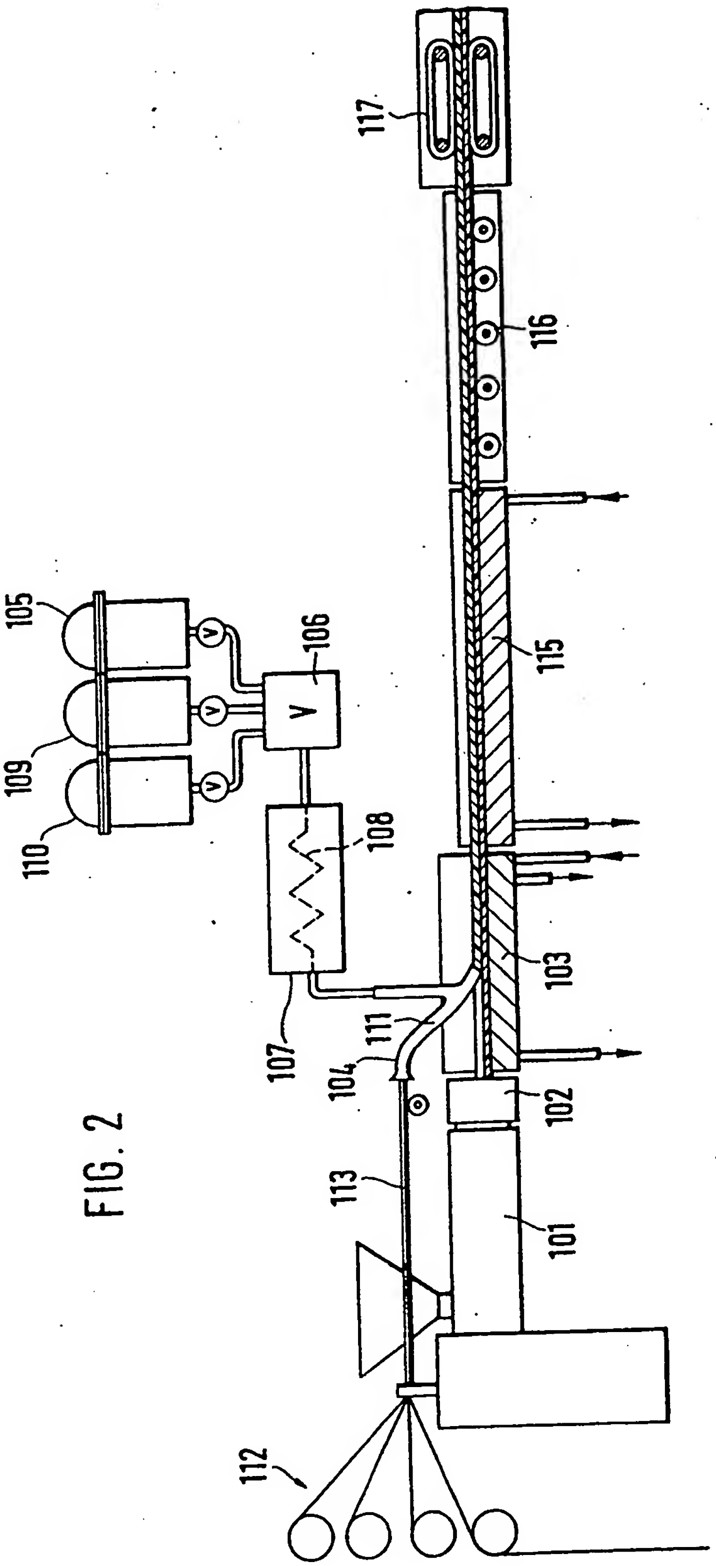

FIG. 2

SPECIFICATION

Process for Manufacturing Bonded Plastics Articles

The invention relates to a process, especially an injection moulding process or extrusion process, for the manufacture of plastic articles having a bonded construction in which at least two plastics having different properties are, during moulding of a plastics article, brought into contact with one another and bonded to one another at a contact surface, with at least one of the two plastics consisting of components which react with one another during moulding, at least in the region of the contact surface, whilst the other plastic is in the liquid state, especially the molten state, in the region of the contact surface.

A process of the type outlined above is described in our earlier Patent Application No. 15164/77 and includes the feature that the joining process, that is to say the process in which different plastics are bonded to one another at one or more contact surfaces, takes place while at least one plastic is in the reactive stage whilst the other, unless it is also undergoing curing, is in the form of a plastic melt. In this context, reaction or reactive stage is to be understood as any state in which identical or different components undergo chemical bonding to one another, thus including, in particular, any type of polymerisation. This achieves a particularly intimate bond between the two plastics of the bonded article, and, according to an advantageous embodiment of the process according to the earlier proposal, the polymerisation progresses to different extents over the thickness of one of the plastics layers. The bonding phenomena which occur at the contact surface have hitherto not been unambiguously elucidated, but it is to be assumed that both a mechanical interlacing and chemical reactions between the bond partners occur and that possibly other physical phenomena (e.g. adhesion) participate.

The present invention is now directed towards an improvement of the process according to the earlier proposal, which contributes to achieving a more intense bond in the region of the contact surface.

The invention accordingly provides a process for the manufacture of a plastics article which comprises bringing at least two plastics into contact with one another and shaping them and bonding them to one another at the contact surface, wherein at least one of the two plastics comprise components which react with one another during the shaping, at least in the region of the contact surface, and the other of the two plastics is in the liquid state during the shaping, at least in the region of the contact surface, and wherein at least one of the said reactive components has a pronounced tendency to diffuse into the other plastic.

As a result of the tendency of at least one component of the reactive plastic to diffuse into the other plastic, the mechanical interlacing between the plastics is intensified and hence leads to greater bond strengths. Advantageous combinations are, for example, those wherein one of the reacting components is a low-molecular weight constituent or a monomer of one plastic and at the same time a solvent for the other plastic. This applies, for example, when processing unsaturated polyesters as the reactive plastic and polystyrene as the other.

In a further embodiment, it can even prove advantageous to employ an excess of the particular component of the reactive plastic which has the pronounced tendency to diffuse. This can have the consequence that copolymerisation reactions and/or grafting reactions occur in the region of the contact surface, so that the bond strength can be controlled by deliberate variation of such reactions.

If, for example, the material combination of unsaturated polyester casting resin and polystyrene is selected for a bonded article, it can be assumed that in the state in which these materials encounter one another when carrying out the process according to the invention, the heat-curing unsaturated polyester resin is in the gel state and consists of the following components: polyester, monomeric styrene, short-chain homopolymerised polystyrene (radical chain polystyrene), copolymerised styrene and possibly also free peroxide radicals. The polystyrene, constituting the second plastic, is present as a melt at about 200°C. The molecular lattice is loosened since intermolecular forces have only a relatively weak effect at this temperature. It is also to be expected that part of the thermoplastic chains are present as chain fragments which are formed, as a result of heat exposure, during any melting and plasticising process.

If now the polystyrene melt encounters the above-mentioned heterogeneous mixture of the reactive phase, the low-molecular weight constituents of this mixture can diffuse, in the gel state, into the polystyrene melt. The diffusion process is substantially favoured by the high mobility of the polystyrene chains in the melt. Monomeric styrene, which is a good solvent for polystyrene even at room temperature, can at the same time penetrate into deeper layers of the reactive phase. This possibility also exists for the short chain radicals and for homopolymer chains. In the further course of the crosslinking of the reactive phase, the constitutents which have penetrated participate in the reaction of the said phase and lead, in the boundary layer, up to a certain depth below the contact surface, to an interlacing in which chains of the two partners of the bond are entangled.

The above-mentioned simultaneously occurring copolymerisation reactions and graft polymerisation reactions between the chain segments of the polystyrene and the resin constituents present in the gel state have the effect of increasing the strength of the bond.

Examples of embodiments are given below in order to illustrate the invention:

Example 1

To produce a bonded article in the shape of a flat sheet of size 110×190×6 mm by the injection moulding process, a three-plate mould with a slide which can be moved into, and out of, the mould cavity was used. The participant plastics used for the bonded article were a thermosetting resin, in the form of an unsaturated polyester resin, and polymethyl methacrylate (PMMA). The thickness of the layer of thermosetting resin should be 4 mm and that of the thermoplastic layer 2 mm.

The unsaturated polyester resin was injected at room temperature into the part of the mould cavity on the clamping side, in which part the mould was kept at a temperature of 150°C. At this point in time, the slide has been introduced into the mould cavity. Following an injection time and holding-pressure time for 110 seconds, a reaction time of 35 seconds was allowed before venting the mould and withdrawing in the slide. This was followed by injecting the PMMA into the part of the mould cavity on the nozzle side, which part was kept at a temperature of 90°C. On entering the mould cavity, the PMMA was at a temperature of about 200°C. After a cooling time of 30 seconds, it was possible to open the mould and to inject the finished bonded article.

The pressures maintained on injecting the polyester resin and the PMMA were 10 bars and about 800 bars respectively.

A bonded article of great strength was obtained, in which the participant plastics were inseparably bonded to one another.

Instead of using pure unsaturated polyester resin, it is readily possible to employ a filled polyester resin. For example, using the same process steps as mentioned above, it is possible to use a reactive phase having the following composition: 100 parts of low profile unsaturated polyester resin (Leguval 7125 from Bayer AG), 100 parts of quartz powder as a filler, 2 parts of peroxide (Trigonox 29B 50 from Akzo-Chemie) and 1 part of coloured pigment.

To carry out the process example described above, the injection moulding machine shown schematically in Figure 1 was used. This comprises two injection units 1 and 2 for the unsaturated polyester resin and the PMMA respectively, arranged with their injection cylinders at right angles to one another. To compound the unsaturated polyester resin, a mixer 3 is provided, which feeds injection unit 1; the PMMA granules are located in a granule dryer 4, from which the granules are conveyed to the injection unit 2. The three-plate mould 5 is shown schematically. The injection moulding machine includes temperature-control instruments 6, the connection of which, for the purpose of maintaining the temperatures of the mould halves mentioned in the Example, is shown in dot-dash lines. A measuring stand 7, for monitoring and recording the process parameters, is provided, and its connection to the parts of the injection moulding machine 1 is also drawn in dot-dash lines.

As a result of the injection units 1, 2 being arranged at right angles to one another, the PMMA is applied at right angles onto the contact surface of the polyester resin layer. Because of the temperature spread of the mould (temperature gradient 60°C), a directional reaction took place in the polyester resin layer, so that the reaction was virtually complete on the wall side during the process of injecting the PMMA, whilst in the region of the contact surface the polyester resin was still in the gel state.

The resulting bonded article 8 is shown schematically.

Example 2

An elongate ribbon-shaped bonded article 42 mm wide and 8 mm thick was produced by an extrusion process. The bonded article possessed a trough-shaped base layer of polystyrene (482 G from BASF AG), made up to a rectangular cross-section by means of a layer, filled into the trough, of unsaturated polyester resin of the same type and composition as in Example 1. The polystyrene was extruded at an extrusion temperature of 170°C; the extrusion rate was 3 meters/minute. The unsaturated polyester resin mixture was supplied by means of a casting device and was applied to the polystyrene base layer immediately behind the nozzle orifice. In this illustrative embodiment, the polyester resin mixture was pre-warmed to a temperature of 90° to 100°C. After bonding of the two plastics, the extruded ribbon was calibrated in a vacuum device, fully cured and cooled.

Figure 2 schematically shows an extrusion installation in which process Example 2, described above, was carried out:

Downstream from a screw extruder 101, having an extruder die 102 for the polystyrene base layer, is located a vacuum and cooling device 103 combined with a feed device 104 for the polyester resin. The polyester resin is supplied to the feed device 104 from a container 105 *via* a valve 106 and a coil 108 located in a heating bath 107. Further containers 109 and 110 contain a cleaning agent and flushing resin, which can be delivered, for the purpose of cleaning the coil 108 and the feed device 104, by appropriately setting the the valve 106.

The feed device 104 possesses a pipe branch 111, through which glass fibre rovings 113 are supplied from an unwind device 112. The glass fibre rovings are impregnated with the polyester resin, supplied through the coil 108, whilst they are still within the feed device 104, and are laid down, together with the polyester resin, on the extruded polystyrene base layer. It is advantageous to pre-warm the glass fibre rovings 113 to match them to the temperature of the polyester resin.

The vacuum and cooling device 103 is

followed by a cooling and reaction zone 115, in which the extrudate is cooled and the polyester resin laminated onto it is cured. Further curing takes place in a subsequent reaction zone 116 in the form of a roller track from which the finished product is then drawn off by means of a caterpillar take-off 117.

Using the process according to the invention, it is even possible to combine relatively brittle plastics with ductile plastics. It has been found that bonding such plastics results in an apparent change in the material characteristics, with the brittle characteristics of one bonding partner being ameliorated, without loss in strength.

The different heat expansion characteristics of the participant materials can be taken into account by suitable selection of the formulation, for example of the monomer system of the reactive plastic, since it is thereby possible to influence the shrinkage characteristics during reaction and match them to the thermal shrinkage characteristics of the other plastic. Possible ways of selecting this formulation are an appropriate choice of the nature and amount of catalysts and/or activators. It is also possible to match the nature and amount of the reactive plastic used to the other plastic. Finally, it is possible to influence the heat expansion characteristics of both the reactive plastic and the other plastic by using suitable fillers and reinforcing agents in a defined amount.

It is also possible to conduct the reaction of the reactive plastic, by suitable temperature control, in such a way as to permit matching to the expansion characteristics of the other bonding partner. For example, it is conceivable to influence the temperature in the interior of the layer which is in the reactive state, by high frequency heating. Such heating also suggests itself if a contact surface in the gel state is to be created on both sides of the layer which is in the reactive state, since with this type of introduction of thermal energy, the higher temperatures occur in the interior of the layer.

The particular matching of the shrinkage characteristics of the bonding partners during the joining process is effected on the basis of the known heat expansion coefficients or shinkage coefficients and on the basis of a knowledge of the shrinkage which occurs during the reaction of the reactive phase.

The pressure and temperature of the participant bonding partners can be set in accordance with experience gathered in processing these partners individually. As far as the pressure is concerned, the general rule is that the pressure is set, in respect of the reactive plastic, so that it exceeds the vapour pressure of the low-molecular weight or monomeric constituents at the particular temperature, in order to prevent these constituents from evaporating. In addition, an elevated pressure may be used in order to allow intermolecular forces to become effective in the region of the contact surface.

Various parameters can be employed to optimise the process according to the invention; the reaction and the interfacial activity, can be most effectively influenced by these parameters. The most suitable parameter to select is the temperature difference by means of which the "gradient" of the reaction in the reactive plastic can be adjusted, as well as the reaction time before joining the partners, that is to say before applying the other plastic, and, finally, also the excess of the particular reactive component which possesses a pronounced tendency to diffuse into the other plastic.

Claims

1. A process for the manufacture of a plastics article which comprises bringing at least two plastics into contact with one another and shaping them and bonding them to one another at the contact surface, wherein at least one of the two plastics comprises components which react with one another during the shaping, at least in the region of the contact surface, and the other of the two plastics is in the liquid state during the shaping, at least in the region of the contact surface, and wherein at least one of the said reactive components has a pronounced tendency to diffuse into the other plastic.

2. A process according to claim 1, wherein one of the said reactive components is a low-molecular weight constituent or a monomer of one of the two plastics, and is at the same time a solvent for the other plastics.

3. A process according to claim 1 or 2, wherein the reactive component having the said pronounced tendency to diffuse is present in excess.

4. A process according to claim 1 substantially as described in the foregoing Example 1 or 2.

5. An injection moulding machine for carrying out the process according to any one of claims 1 to 4, with at least two injection units, wherein the mould has at least one removable slide which subdivides the mould cavity into two part-cavities and in that the injection units are each in communication with one of the part-cavities.

6. A machine according to claim 5 substantially as described with reference to Figure 1 of the accompanying drawings.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1979. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.